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(54) Mineral oils

(57) Lubricating oil basestocks are prepared by subjecting a petroleum vacuum distillate fraction or residue to a process including solvent extraction followed by mild catalytic

hydrogenation at 310—450°C followed by de-waxing.

The resulting basestocks have low viscosities, low volatilities and high viscosity indices and are suitable for use in the formulation of "energy saving oils".

GB 2 059 433 A

SPECIFICATION

Production of mineral oils

The present invention relates to a process for the production of mineral oils with a high viscosity index and a low viscosity and which possess improved volatility and resistance to oxidation as compared with conventional paraffinic oils of similar viscosities. 5

To comply with the demands of lubricating oil consumers, oil refiners have developed lubricating oils having high viscosity indices. Moreover, certain applications demand oils with good resistance to oxidation and low volatility.

The resistance to oxidation of an oil makes it possible to use the oil in an oxidising atmosphere and at a relatively high temperature with reduced formation of acidic decomposition products which are often corrosive and the precursors of undesirable insoluble gums. 10

The volatility of an oil is connected with the loss of light components initially present in the oil, as a result of a rise in temperature. This phenomenon causes lubricant losses which are prejudicial to the user and also in certain cases may appreciably modify the viscosity of the oil.

A relationship exists for oils prepared according to conventional refining processes between the viscosity of the oil and its volatility. The latter increases as the viscosity diminishes. It is thus difficult to obtain a mobile mineral oil having a low volatility. The present tendency is now to use oils with a low viscosity having a high viscosity index and a low degree of volatility of lubricating engines. Such oils are known as "energy saving oils". They facilitate cold starting of the engine and reduce losses of oil by evaporation when the engine is running. Synthetic lubricants prepared from diesters and poly- α -olefins possess the properties required by energy saving oils, but they are expensive to produce. 15 20

Processes for preparing low-viscosity oils with a high viscosity index from petroleum fractions are known. For example, it is possible to prepare such oils by fractionating a hydrocracking residue in vacuo followed by de-waxing. In certain cases a fraction of the hydrocracking residue is treated beforehand with a selective solvent, e.g. furfural or phenol. Another process comprises hydrogenating a petroleum fraction under severe conditions and then subjecting it to treatment with a selective solvent followed by a de-waxing process. Finally, by retaining a conventional sequence of process stages for preparing lubricants, e.g. vacuum distillation, solvent extraction, de-waxing and finishing treatment, low viscosity oils with a high viscosity index can be obtained by increasing appreciably the severity of the selective solvent treatment. 25 30

All these processes have the disadvantage of providing comparatively low yields of oil in relation to the distillate or the hydrocracking residue feedstock.

The Applicants have now discovered that if between the selective solvent extraction stage and the de-waxing stage a mild raffinate hydrogenation stage is interposed, then it is possible to prepare in a good yield lubricants having a high viscosity index, a low viscosity, a low degree of volatility and an improved resistance to oxidation. 35

Lubricants prepared according to the invention have a lower volatility at an equivalent viscosity than those prepared by a solvent treatment under severe conditions.

Thus, according to the present invention there is provided a process for the production of a lubricating oil basestock which process comprises subjecting a petroleum vacuum distillate fraction or residue to a solvent extraction process to produce a paraffinic raffinate having a viscosity between 3.5 and 31 cSt at 100°C, subjecting the raffinate to a mild catalytic hydrogenation treatment under the following conditions: 40

Temperature °C : 310 — 450

Pressure (bars ga) : 30 — 100 45

Feedstock Space Velocity LHSV : 0.25 — 3

H₂:Hydrocarbon ratio : 100:1 — 500:1

(H₂ at NTP, Hydrocarbon at 20°C)

and subjecting the hydrogenated raffinate to a de-waxing process and, optionally, to a finishing treatment. 50

Solvent extraction, de-waxing and finishing treatments are well known, conventional processes.

Treatment by selective solvent, e.g. furfural or phenol, reduces the concentration of undesirable compounds, mainly polyaromatics and aromatic sulphur compounds. The hydrogenation which follows therefore affects in particular monoaromatic, diaromatic and sulphur compounds remaining in the raffinate. The flexibility of the hydrogenation process, whilst minimising the proportion of sulphur compounds which inhibit oxidation, makes it possible to re-establish an optimum balance of sulphur/aromatic compounds which is indispensable for good resistance to oxidation of the 55

hydrogenated oil. The process according to the present invention therefore makes it possible to treat petroleum fractions derived from a high sulphur crude oil and to obtain in good yield lubricating oil basestocks containing very little sulphur but having a good resistance to oxidation.

For the preferred operation of the processes according to the present invention, catalytic

5 hydrogenation of the raffinates is carried out under the following conditions: 5

— at a temperature between 380 and 400°C

— at a space velocity between 1 and 1.5 volume of feed per volume of catalyst per hour.

The catalyst utilised is a known catalyst for hydrogenating aromatic hydrocarbons. It contains a metal of Group IV of the Periodic Table and one or more metals of Group VIII deposited on an alumina

10 support. Preferred catalysts contain oxides of molybdenum and nickel or cobalt, e.g. 10

MoO₃ : 14% by weight

NiO : 3% by weight

Support : Alumina

In putting into effect the process according to the invention, the catalyst is activated by a sulphur 15 compound according to conventional methods, e.g. hydrogen sulphide, carbon disulphide or sulphur 15 compounds in the feedstock. This activation is carried out in situ at a temperature in the vicinity of the reaction temperature. The raffinate to be treated passes over the catalyst with the hydrogen. The hydrogenated product is then separated from the gases and treated with steam to eliminate hydrogen sulphide and light products formed during hydrogenation.

20 The process described in the present invention is of general application to paraffinic raffinates 20 whatever the origin of the crude.

The paraffinic raffinates treated according to the process of the invention preferably have an aromatic content from 10 to 35% by weight (ASTM D 2007 method).

The heavier the feedstock, the greater is the decrease in viscosity of the raffinate following 25 hydrogenation. But surprisingly, this gain in mobility occurs without any appreciable increase in 25 volatility.

The process of the present Application is advantageously applied to the production of base oils with a high viscosity index, i.e. greater than 95. These base oils serve for the preparation of high-performance industrial oils, e.g. transformer oils, transmission oils and coolant fluids. These oils require 30 to be resistant to oxidation and possess low viscosities at low temperatures. 30

The process is also applied advantageously to the production of engine oils utilised in crankcases, gearboxes, axles, etc. of petrol or diesel engines. The properties required here are good viscosity properties at high and low temperatures, good resistance to oxidation and low volatility. This is the category of lubricants to which the "energy saving oils" belong.

35 Finally the process according to the invention may be applied to basestocks utilised in oils for 35 implementing polymerisation processes (process oils).

For these applications the basestocks obtained may be utilised as produced or in admixture with other known basestocks.

The basestocks obtained by the process of the present invention have viscosities, after de-waxing, 40 between 3 and 28 cSt at 100°C. By mixing with a conventional, more viscous base, it is possible to 40 decrease the viscosity of the latter without lowering its volatility.

Furthermore, it has been discovered that basestocks prepared according to the process described in the present invention fully respond to conventional additives utilised in the formulations of industrial oils and engine oils.

45 The invention is illustrated with reference to the following examples. 45

EXAMPLE 1

A raffinate (No. 1) obtained by furfural extraction of a vacuum distillate fraction derived from a Kuwait crude was hydrogenated.

Properties of the raffinate were as follows:

Raffinate No. 1

	Density at 70°C	0.8324	
	Viscosity at 100°C	4.88 cSt	
	% Sulphur by weight	0.89	
5	Refractive index at 68°C	1.4617	5
	% of aromatics (ASTM D2007 method)	28.2	

This raffinate was hydrogenated over a hydrogenation catalyst of the following composition:

	MoO ₃	13.9 % wt	
10	NiO	3.1 % wt	10
	Support	alumina, previously sulphided.	

The hydrogenated product was subjected to a light vacuum distillation to eliminate the light products formed during hydrogenation (topping). The raffinate hydro-treated in this way was de-waxed by means of a mixture of methylisobutylketone (85%) and methylethylketone (15%).

15 The hydrogenation conditions selected and the results obtained are shown in Table 1 where the yields and qualities of the products obtained according to the process of the Invention are compared with those resulting from a conventional process. 15

Thin-layer chromatography analyses on IATROSCAN S-2 apparatus carried out on the raffinate before and after hydrogenation show that hydrogenation affected 81% of the polyaromatic compounds present in the raffinate and 28% of the monoaromatic compounds. 20

TABLE 1 — HYDROGENATION OF RAFFINATE NO. 1

HYDROGENATION Conditions	Pressure bar	85									
		150					150				
		1.5		1		1		1		1	
H ₂ /raffinate vol/vol		400°C		360°C		360°C		380°C		400°C	
Vol/vol/Hr.											
Temperature											
Yield % in relation to the raffinate (weight) after topping		92.7		97.1		94.6		90.7			
Density at 70°C		0.8183		0.8206		0.8203		0.8165			
Viscosity at 100°C cSt		4.29		4.48		4.49		4.25			
% sulphur by weight		0.07		0.06		0.08		0.06			
Refractive index at 68°C		1.4551		1.4559		1.4554		1.4558			
% aromatics (ASTM D2007)		24						22.6			
Dewaxing temperature		-15°C	-24°C	-15°C	-24°C	-15°C	-24°C	-15°C	-24°C	-15°C	-24°C
Yield		83.6	80.6	84	81	84.2	79.3	82.7	78	82.7	78
Density at 15°C		0.863	0.866	0.866	0.864	0.863	0.865	0.861	0.863	0.861	0.863
Refractive index at 20°C		1.477	1.478	1.4768	1.4778	1.4765	1.4772	1.477	1.4778	1.477	1.4778
Viscosity at 100°C cSt		4.50	4.56	4.78	4.86	4.74	4.79	4.50	4.515	4.50	4.515
Viscosity at 40°C cSt		25.53	24.10	25.89	26.92	25.43	26.44	23.04	23.53	23.04	23.53
Pour Point		-11	-21	-11	-22	-12	-20	-12	-24	-12	-24
Corrected VI		105	102.2	103.7	102	105.2	102.3	107	105	107	105
Noak volatility (1 hr, at 250°C)			16.9		15.7						
% aromatics (ASTM D2007)		28.5	30				15.3	26.8	15.5	26.8	29
ANALYSIS OF THE FINISHED PRODUCT AFTER DEWAXING											

HYDROGENATION
Conditions

ANALYSIS OF THE FINISHED
PRODUCT AFTER DEWAXING

The determination of losses of oil by evaporation is effected according to the Noak DIN 51.581 method. The values indicated correspond to the losses in weight calculated after the oil has been maintained for one hour at 350°C. Resistance to oxidation is evaluated according to the IP 306 method. The oil is brought into contact for 48 hours at 120°C with oxygen in the presence of a catalyst (copper).

5 The content of TOP % oxidation products and the weight of deposits in % are determined. 5

It can be seen from the Table that a decrease in the space velocity or an increase in the hydro-treating temperature is expressed in a significant decrease in viscosity and increase in viscosity index.

By comparison with a base obtained from the same raffinate but by a conventional process, it is noted that the process of the present invention leads to more mobile bases having viscosity indices appreciably higher and volatility and oxidation behaviour which are comparable. 10

EXAMPLE 2

The process was applied to a raffinate (No. 2) obtained by furfural extraction of a vacuum distillate fraction derived from a Kuwait crude. The raffinate had the following properties:

Raffinate No. 2

15	Density at 70°C	0.8460	15
	Viscosity at 100°C	9.9 cSt	
	Refractive index at 68°C	1.4680	
	% aromatics (ASTM D 2007)	12.8	

20 This raffinate was subjected to hydrogenation and a sequence of treatments identical to those in Example 1. The hydrogenation conditions and the results obtained are shown in Table 2, where the yields and qualities of the products obtained according to the process of the present invention are compared with those of a conventional process. 20

Thin layer chromatography analysis on an IATROSCAN S-2 apparatus carried out on the raffinate before and after hydrogenation showed that hydrogenation affected 75% of the polyaromatic compounds present in the raffinate and only 3% of the monoaromatics. 25

EXAMPLE 3

A raffinate (No. 3) obtained by furfural extraction of a vacuum distillate derived from Zakum crude was hydrogenated. The properties of the raffinate were as follows:

Raffinate No. 3

30	Density at 70°C	0.8247	30
	Viscosity at 100°C	4.87 cSt	
	Refractive index at 68°C	1.4590	
	% aromatics (ASTM D 2007)	27.5	

35 This raffinate was subjected to the sequence of treatments described in Example 1: hydrogenation, topping, de-waxing. 35

The hydrogenation conditions, the results obtained and a comparison with the products obtained by a conventional process are summarised in Table 3.

TABLE 2
HYDROGENATION OF RAFFINATE No. 2

HYDROGENATION Hydrogenated Product Conditions	Pressure, bar	35	NON-HYDRO- TREATED RAFFINATES	
	H ₂ /raffinate, vol/vol	150		
	vol/vol/hr.	0.5		
	Temperature	400°C		
	Yield, % in relation to the raffinate (by weight)	86.7		
	Density at 70°C	0.8260		
	Viscosity at 100°C, cSt	7.07		
	Refractive index 68°C	1.4629		
	% aromatics (ASTM D 2007)	11.5		
ANALYSIS OF THE FINISHED PRODUCT AFTER DE-WAXING	De-waxing temperature	-12°C	-12°C	
	Yield % by weight	73%	80.6%	
	Density at 15°C	0.871	0.887	
	Refractive index at 20°C	1.4837	1.4885	
	Viscosity at 100°C, cSt	7.45	10.5	
	Viscosity at 40°C cSt	49.15	95	
	Pour point	-9	-11	
	Corrected VI	114	95.2	
	Noak volatility, %	6.2	3	
	% aromatics (ASTM D 2007)	14.6	17.1	
				Specifications
	Resistance to TOP %	0.14	0.48	< 1
	oxidation, IP 306 % deposits	2.4	0.7	<10

TABLE 3
HYDROGENATION OF RAFFINATE No. 3

HYDROGENATION Conditions Hydrogenated Product	Pressure, bar	35		NON-HYDRO- TREATED RAFFINATES
	H ₂ /raffinate, vol/vol	150		
	Temperature	400°C		
	vol/vol/hr.	1.5	1	
	Yield % in relation to the raffinate (by weight)	91.2	89.5	
	Density at 70°C	0.8159	0.8138	
	Viscosity at 100°C, cSt	4.37	4.28	
	Refractive index at 68°C	1.4555	1.4548	
% aromatics (ASTM D 2007)	21.5	19.9		
ANALYSIS OF THE FINISHED PRODUCT AFTER DE-WAXING	De-waxing temperature	-12°C	-12°C	-12°C
	Yield % by weight	78	76	77.3
	Density at 15°C	0.863	0.861	0.873
	Refractive index at 20°C	1.4775	1.4770	1.4830
	Viscosity at 100°C, cSt	4.65	4.57	5.13
	Viscosity at 40°C, cSt	25.46	24.29	30.9
	Pour point	-10	-10	-10
	Corrected VI	108.4	113.4	103.3
	% aromatics (ASTM D 2007)	27.5	26.2	35.5

EXAMPLE 4

The process described in Example 1 was applied to a raffinate (No. 4) obtained by furfural extraction of a vacuum residue derived from Zakum crude, the residue having been previously de-asphaltised with propane.

The properties of the raffinate were as follows:

Raffinate No. 4

Density at 70°C	0.865
Viscosity at 100°C	26.72 cSt
Refractive index at 68°C	1.4800

As in Example 1 this raffinate was subjected to catalytic hydrogenation, topping and de-waxing. The hydrogenation conditions, the results obtained by analysis of the products and a comparison with the products obtained by a conventional process are summarised in Table 4.

TABLE 4
HYDROGENATION OF RAFFINATE No. 4

HYDROGENATION Conditions Hydrogenated product	Pressure, bar	35	NON-HYDRO- TREATED RAFFINATES
	H ₂ /raffinate, vol/vol	150	
	vol/vol/hr.	0.5	
	Temperature	400°C	
	Yield, % in relation to the raffinate (by weight)	87.2	
	Density at 70°C	0.847	
	Viscosity at 100°C, cSt	16.75	
	Refractive index at 68°C	1.4718	
ANALYSIS OF THE FINISHED PRODUCT AFTER DE-WAXING	De-waxing temperature	-12°C	-12°C
	Yield, % by weight	74.3	76.6
	Density at 15°C	0.887	0.908
	Refractive Index at 20°C	1.4945	1.5002
	Viscosity at 100°C cSt	17.18	31.22
	Viscosity at 40°C, cSt	174.20	480.66
	Pour point	-12	-12
	Corrected VI	106.6	93.1

CLAIMS

1. A process for the production of a lubricating oil basestock which process comprises subjecting a petroleum vacuum distillate fraction or residue to a solvent extraction process to produce a paraffinic raffinate having a viscosity between 3.5 and 31 cSt at 100°C, subjecting the raffinate to a mild catalytic hydrogenation treatment under the following conditions:

Temperature °C : 310 — 450

Pressure bars (ga) : 30 — 100

Feedstock Space Velocity LHSV : 0.25 — 3

H₂:Hydrocarbon Ratio : 100:1 — 500:1

(H₂ at NTP, Hydrocarbon at 20°C)

and subjecting the hydrogenated raffinate to a de-waxing process.

2. A process according to claim 1 wherein the hydrogenation catalyst comprises a metal of Group VI of the Periodic Table and one or more metals of Group VIII deposited on an alumina support.

3. A process according to claim 2 wherein the catalyst comprises oxides of molybdenum and nickel or cobalt.

4. A process according to any of the preceding claims wherein the hydrogenation catalyst is activated by presulphiding.

5. A process according to any of the preceding claims wherein the hydrogenation feedstock is a paraffinic raffinate having an aromatics content in the range 10 to 35% by weight.

6. A process for the production of a lubricating oil basestock according to claim 1 as hereinbefore described with reference to any one of the Examples.

5 7. Products whenever prepared by a process according to any of the preceding claims. 5

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